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PREPARATION OF OIL SAND COKE - WATER SLURRY FOR ENTRAINED BED GASIFIER USING ULTRASONIC TREATMENT.

Executive Summary
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EXECUTIVE SUMMARY

The upgrading of Athabaska oil sands bitumen involves a coking process. Currently the Suncor plant employs a delayed coking technique and a fluid coking process is used by the Syncrude plant. The by-product coke contains about 80% carbon. However, direct combustion of this material is precluded by the high levels of sulfur, vanadium and other transition metals that it contains. Large quantities of the coke are now being stockpiled at the plant sites until it can be economically used.

The energy content of this material might be recovered through gasification rather than direct combustion. This would reduce the amount of off-site energy, particularly natural gas, that is consumed by the upgrading plants. Furthermore, the product gas might be used as a feedstock for other processes such as liquifaction. High gasification conversions can be achieved in an entrained bed reactor. A slurry feeding system would increase the flexibility of this type of reactor, but the operation of such a system depends on the stability and pumpability of the feed slurry. Additives such as surfactants and stabilizers can be used to control these properties.

In view of the above, an evaluation of the efficacy of several additives and some methods for aqueous coke slurry preparation was carried out. The additives that were examined in this work included: commercial surfactants, materials that are now classified as industrial wastes, and stabilizers such as natural gums and Wyoming bentonite. Additionally, an

assessment was made of the advantages of intense ultrasound as a mixing process over conventional mechanical mixing.

Surfactants are known to enhance wetting of solid surfaces by liquids. This is achieved by lowering the contact angle of the liquid on the solid surfaces. It was believed that enhanced wetting is a major part of the role that is played by surfactants in slurry preparation. Thus, the contact angles of several liquids were measured on Syncrude fluid coke.

This was achieved by observing the rate at which the liquids wet the coke while rising in a tube packed with coke, and then applying the Washburn-Rideal equation. The results indicate that the coke is not wet significantly better by a given liquid than it is by water unless its surface tension is lower than 30 dyne cm^{-1}. Moreover, a liquid will not wet the coke completely unless it has a surface tension below 25 dyne cm^{1}. The common commercial surfactants studied in this work did not lower the surface tension of aqueous solutions below 39 dyne cm^{-1} and did not give contact angles much different than that obtained with water ($68 \pm 5°$). Exotic fluorocarbon and silicone based surfactants were found to produce aqueous solutions with surface tensions as low as 16.8 dyne cm^{-1}. Such solutions were able to yield contact angles of 32° using the fluorocarbon based surfactant and 39° using the silicone based surfactant. However, these surfactants are too costly for large scale use in slurries. The more common commercial surfactants that were studied in

this work are widely used in slurry preparation, where they have yielded large improvements in the properties of slurries. It is therefore unlikely that enhanced wetting is a major function of surfactants in slurry preparation.

The major function of surfactants used in slurry preparation is the suppression of particle flocculation. Flocculation yields a three dimensional network that resists sedimentation. However, this: reduces the maximum solids concentration that is achievable in a given slurry, can yield an excessively viscous slurry, and is a departure from the dispersed state which was the purpose of grinding and mixing. Furthermore, the slurries become increasingly susceptible to sedimentation as the concentration of surfactant is increased, and in extreme cases, highly compact and dilatant sediments are obtained. This can be attributed to a reduction of the stabilizing influence of flocculation. Consequently, stabilization must be provided by other means such as the use of a stabilizer.

An assessment of the consistency of several oil sands coke slurries was achieved using a modified rod penetration test. This test yielded a parameter that showed a non-linear dependence on: the settling time, concentration and nature of any additives, and the coke concentration of the slurries. The results showed that most of the commercial additives significantly improved the stability of slurries, but none of the six waste materials tested improved stability. In fact slurries with coke

concentrations much above 60 wt% can only be prepared if a surfactant is added.

The existence of an optimum concentration of surfactant and stabilizer was also indicated. Slurries that were prepared with the optimum concentration of additives showed the best combination of static stability and fluidity. Under these conditions, stable slurries containing up to 70 wt% Syncrude coke (50% passing through a 200 mesh screen) could be prepared. Generally speaking, as the coke concentration increases, the optimum concentration of surfactant that is required increases while the optimum concentration of stabilizer that is required decreases. Employing concentrations of additives in excess of the optimum concentration for a given slurry is not only wasteful but can even be counterproductive. The suitability of any combination of additives can only be determined by experiment.

Three particle size distributions of Syncrude coke containing 25%, 50% and 80% -200 mesh particles were examined to determine the effect of particle size on slurry stability. It was found that the concentration of stabilizer that was required to yield a fluid slurry increased as the relative fraction of coarse particles was increased.

Finally, it was determined that intense ultrasound was more effective as a mixing method than mechanical mixing with a Waring blender only for slurries with coke concentrations below 60 wt%. Excessive sound

absorption produced rapid heating and ineffective mixing if ultrasound was applied when the coke concentration was 60 wt% or higher. The minimum mixing time was about 15 min. If shorter mixing times were employed, air was not effectively displaced from the coke surfaces and bubbles formed in the slurry after standing some time.

RESUME

La bonification des huiles des sables bitumineux de l'Athabaska nécessite un procédé de cokéfaction. Présentement, Suncor se sert d'une technique de cokéfaction différée tandis qu'un procédé de cokéfaction fluide est utilisé pour Syncrude.

Le sous-produit de coke contient près de 80% de carbone, malgré cela sa combustion directe n'est pas conseillée due à la haute teneur en soufre, en vanadium et autres métaux de transition. De grandes quantités de ce coke sont maintenant empilées aux sites d'exploitation en attendant d'être utilisé économiquement.

Le contenu énergétique de ce matériel pourrait tout de même être récupéré par gazéification plutôt que par combustion directe. Ceci réduirait la quantité d'énergie venant de l'extérieur, le gaz naturel notamment, consommée par les usines de bonification. Sans compter que les produits gazeux peuvent servir de charge d'alimentation pour des procédés comme la liquéfaction, par exemple. Il est possible d'obtenir de bons rendements de conversion énergitique avec un réacteur à entraînement sur tapis roulant. Pour augmenter la flexibilité d'un tel réacteur, il serait souhaitable d'amener la charge de coke sous forme de suspensions. L'opération d'un tel système dépend surtout de la stabilité et de la facilité à pomper les

suspensions de coke. Pour contrôler ces propriétés, des agents tensioactifs et des stabilisateurs peuvent être ajoutés.

Ce rapport présente une évaluation de l'efficacité de plusieurs additifs et de certaines méthodes de préparation de suspension de coke en solutions aqueuses. Les additifs examinés incluent des agents tensioactifs commerciaux, des substances encore considérées déchets industriels, et des stabilisateurs tels des gommes naturelles et de la bentonite du Wyoming. L'étude a aussi porté sur l'évaluation des ultrasons comme moyen de mélange au lieu d'un mélangeur mécanique conventionnel.

Les agents tensioactifs sont réputés pour améliorer le mouillage des surfaces des liquides. Ceci est relié au fait que les agents tensioactifs diminuent l'angle de contact des liquides sur les solides. On croyait que le principal effet des agents tensioactifs sur les suspension de coke était de faciliter le mouillage du coke. Par conséquent, les angles de contacts de plusieurs liquides ont été mesurés sur des particules de coke de Syncrude.

Les angles de contact ont été mesurés en appliquant l'équation de Washburn-Rideal à partir du taux de mouillage du coke lorsque le liquide monte dans un tube plein de particules de coke. Les angles de contact obtenus indiquent que le coke

n'est pas mouillé plus efficacement par l'eau pure que par un liquide donné sauf si sa tension superficielle est inférieure à 30 dynes cm^{-1}. D'ailleurs, un liquide ne mouillera pas complètement les particules de coke à moins que sa tension superficielle ne soit inférieure à 25 dynes cm^{-1} . La tension superficielle des solutions aqueuses n'atteignait jamais moins de 39 dynes cm^{-1} en utilisant les agents tensioactifs commerciaux les plus communs ; les angles de contact ne différaient pas beaucoup de celui de l'eau pure (68 ± 5^{o}) non plus. Des agents tensioactifs plus exotiques à base de fluorocarbone et de silicone ont permis d'obtenir des solutions aqueuses dont la tension superficielle peut descendre jusqu'à 16.8 dynes cm^{-1}. Les angles de contact de ces solutions peuvent atteindre 32^{o} dans le cas des agents tensioactifs à base de fluorocarbone et 39^{o} pour ceux à base de silicone. Par contre, ces agents tensioactifs plus rares sont trop coûteux pour un usage à grande échelle. Ceci dit, il faut noter que les agents tensioactifs commerciaux étudiés pour ce projet sont couramment utilisés, avec succès, dans la préparation de suspensions de coke. Il est donc peu probable que se soient l'amélioration des propriétés mouillantes qui justifie l'emploi des agents tensioactifs pour la préparation des suspensions de coke.

On a recours à d'autres additifs que les agents tensioactifs pour assurer la stabilité des solutions car les

suspensions ont tendance à sédimenter de plus en plus rapidement à mesure que la concentration en agents tensioactifs augmente. A forte concentration d'agents tensioactifs, la floculation perd toute son action stabilisante. Dans les cas extrêmes, on obtient des sédiments très compacts et dilatants. La fonction la plus importante des agents tensioactifs dans la préparation des suspensions est de supprimer la floculation. La floculation crée un réseau tri-dimensionel qui résiste à la sédimentation; l'état disperseé n'est plus le même et l'on s'éloigne du but premier qui était de broyer et de mélanger. La concentration maximum des solides dans la suspension doit être réduite et les suspensions peuvent devenir excessivement visqueuses.

La consistance de plusieurs huiles de suspensions de coke a été évaluée en employant un test modifié de pénétration de bâton. De ce test, on extrait un paramètre qui varie d'une façon non-linéaire selon 3 variables: le temps de sédimentation, la concentration et la nature des additifs , et la concentration des particules de coke en suspension. Les résultats démontrent que la plupart des additifs commerciaux, contrairement à chacun des 6 déchets industriels, améliorent la stabilité. En fait, des suspensions dont la concentration en coke dépasse 60% (poids) n'ont pu être obtenus que par l'addition d'agents tensioactifs.

Il a été possible d'établir des conditions optimales de concentration d'agents tensioactifs et de stabilisateurs. Les suspensions préparées avec de telles concentrations d'additifs procuraient la meilleure combinaison de stabilité et de fluidité. Des suspensions stables contenant jusqu'à 70% (poids) de coke de Syncrude (dont 50% des particules passent au travers d'un tamis de 200 *mesh*) ont pu être préparées avec succès suivant ces conditions. Généralement, à mesure que l'on augmente la concentration de coke dans une suspension, il faut augmenter la concentration d'agents tensioactifs et diminuer la concentration de stabilisateurs pour obtenir des conditions optimales. L'excès d'additifs ne conduit pas seulement au gaspillage mais s'avère aussi improductif. La combinaison idéale d'additifs peut seulement être établi d'une façon empirique.

Pour déterminer l'effet de la grosseur des particules sur la stabilité des suspensions, trois types d'échantillons de coke de Syncrude ont été examinées. Chaque échantillon contenait 25%, 50% ou 80% de particules de 200 *mesh*. Les résultats indiquent que la concentration du stabilisateur doit augmenter proportionnellement avec la fraction relative des particules pour conserver la fluidité à une suspension de coke.

Finalement, le mélange avec les ultrasons s'est avéré plus efficace que le mélangeur mécanique Waring uniquement lorsque

la concentration des suspensions est inférieure à 60% (poids). L'absorption excessive des sons résulte en un échauffement rapide et un mélange inégal s'ensuit. Le mélange durait au moins 15 minutes. Autrement, l'air à la surface du coke n'était pas désorbé efficacement et des bulles se formaient lorsque la suspension avait reposé pendant un certain temps.

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ABSTRACT

An assessment was made of the effect of a combination of the surfactant PLURONIC F108 with each of three stabilizers (Wyoming bentonite, xanthan gum and guar gum) on the storage properties of aqueous slurries containing 60 wt% oil sand coke. This was accomplished using a modified rod penetration test. Such tests revealed the existence of an optimum concentration of each additive. Slurries that were prepared with the optimum concentration of additives showed the best combination of static stability and fluidity. Three particle size distributions of Syncrude coke were examined to determine the effect of particle size on slurry stability. It was found that the concentration of stabilizer that was required to yield a fluid slurry increased as the relative fraction of coarse particles was increased.

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CHAPTER 8
FURTHER EVALUATION OF OIL SANDS COKE SLURRIES

8.1 Recent Developments In Slurry Preparation

The objective of this section is to update section 1.5 ("Surfactants Currently Used In Slurry Preparation") of reference (1). The vast bulk of recent work has been covered by the Japanese patent literature. Much of this work has dealt with methods for slurry preparation such as wet grinding of coal used in slurries (2-4). Intense ultrasound with a frequency of 19 kHz has been employed to produce a stable aqueous coal slurry (5). The resulting slurry contained 68 wt% coal (75 % passing 200 mesh)) and 0.80 wt% anionic surfactant. This slurry was stable for more than four weeks while identical slurries produced without ultrasound were unstable.

The particle size distribution has been found to be a significant factor in determining the rheology of slurries (6-9). It has been suggested that particles with diameters smaller than 45 μm (ie.-325 mesh particles) comprise 20 to 35 % of particles in an optimum particle size distribution (7,9). It is believed that such fine particles find their way into the interstices between large particles where they act in a manner that is analogous to ball bearings (7). This causes a reduction in the shear force that is required to make the mixture flow. If the relative fraction of these fine particles is increased above 35 %, the

viscosity of the mixture increases sharply. In this case the internal friction increases because the fine particles can no longer act as "ball bearings" (7). It is also suggested that tight control of size distribution on a large scale is more difficult than simply using additives to control slurry rheology (7).

Additives have been the subject of a large fraction of recent work on aqueous fuel slurries (7,10-16). Some of these materials such as kaolin clay (10) and chemically modified methyl cellulose (11) can be considered to be storage stabilizers. Several surfactants have also been covered in the Japanese patent literature (12-16). Nonionic surfactants are generally some type of long chain polyalkaleneoxide ether derivative (12-14). Anionic surfactants that have been discussed in this literature are usually some type of long chain aryl sulfonate derivative (15). Weak, low cost lignosulfonates have been used to reduce the amount of expensive naphthalene sulfonate employed in the preparation of an aqueous coal slurry (16). In this work as much as 50 % of the naphthalene sulfonate could be replaced with lignosulfonate without deterioration of the slurry properties.

It has also been reported that pH can influence the rheology of aqueous coal slurries (7,17). The pH of slurries with the lowest viscosity was found to be in the range 8.3 to 11.35 (17) or 8.5 to 9.5 (7). It was found that bases with multivalent anions such as $(PO_3)^{-3}$ and $(CO_3)^{-2}$ are most effective in reducing slurry viscosity (17). It is assumed that coal

strong particle aggregation is prevented by an increase in the electrostatic repulsion between particles in the optimum pH range (7).

8.2 Materials And Methods

8.2.1 Reagents

8.2.1.1 Coke

Dry ground Syncrude fluid coke (see ref. (1)) was used in the preparation of most of the test slurries. However, Syncrude coke samples with two other particle size distributions were also prepared. These samples were prepared by adding either -200 mesh or 60x200 mesh Syncrude coke to dry ground Syncrude coke. About 80 wt% of the particles were able to pass through a 200 mesh screen in one of these particle size distributions while only 25 wt% were able to do so in the second particle size distribution. The sieve analysis of these samples and the original dry ground Syncrude coke are given in table 8.1.

For the rest of this work they will be identified by the relative size of the -200 mesh fraction. Thus, original dry ground Syncrude coke will be referred to as "50% -200 mesh" Syncrude coke and the other two samples will be referred to as "25% -200 mesh" and "80% -200 mesh" Syncrude coke.

A sample of Suncor delayed coke was also obtained from CANMET Energy

Research Laboratories, Ottawa. A chemical analysis of this material is given in table 8.2. The Suncor coke was ground at CANMET using an apparatus and method that was identical to that used to grind the Syncrude coke (see ref. (1)). The sieve analysis of this material is given in table 8.3.

8.2.1.2 Additives

On the basis of past work (1,18,19), PLURONIC F108 (B.A.S.F Canada Inc.) was selected as the most effective surfactant. Thus, it was the only surfactant employed in the present work. The following stabilizers were also employed: Wyoming bentonite, xanthan gum and guar gum. These materials are described in reference (19).

8.2.2 Methods

8.2.2.1 Slurry preparation

All slurries were prepared and stored as described in reference (19) with the following exceptions:

(1) Mechanical mixing was provided by a Hamilton Beach "Drinkmaster" disperser. This inexpensive device seemed to be as effective as the Waring blender that had been used previously but was easier to clean. This allowed more slurries to be prepared than would have been possible using the Waring blender.

Table 8.1 Sieve analysis of three particle size distributions of Syncrude coke.

SIZE CONSIST	FRACTION OF TOTAL MASS "25% -200 MESH" wt%	"50% -200 MESH" wt%	"80% -200 MESH" wt%
+80	24.4	4.9	2.1
80x100	22.7	14.6	4.9
100x120	3.3	2.4	1.6
120x170	19.3	18.9	6.4
170x200	5.4	8.7	3.3
-200	25.0	50.4	81.5

Where 80x100 means the sample passed an 80 mesh screen but not a 100 mesh screen.

Table 8.2 Analysis of Suncor delayed coke.*

ANALYSIS	RESULT wt%
Ash	3.8
Volatile	12.5
Fixed carbon	83.7
Carbon	83.7
H	3.7
S	5.7
O (by diff.)	1.3
SiO_2	42.18
Al_2O_3	22.75
Fe_2O_3	11.85
NiO	1.21
V_2O_5	4.40
TiO_2	3.28
CaO	5.01
MgO	1.96
BaO	0.03

* reference (20).

Table 8.3 Sieve analysis of Suncor coke.

SIZE CONSIST	FRACTION OF TOTAL MASS wt%
+80	0.1
80x100	2.6
100x120	0.5
120x170	6.7
170x200	5.7
-200	84.3

Where 80x100 means the sample passed an 80 mesh screen but not a 100 mesh screen.

A fixed mixing time of 15 min was employed in this work.

(2) Only 60 wt% slurries were prepared.

(3) The coke was added in one batch since the gradual addition of coke that was previously employed seemed to make little difference.

8.2.2.2 Penetration test

The apparatus and procedure that was used to evaluate the consistency of the sediment in each slurry was identical to that described in reference (19). However slurries were tested after 48 h only since slurries to be used for gasification would not be stored for periods of time much in excess of 24 h.

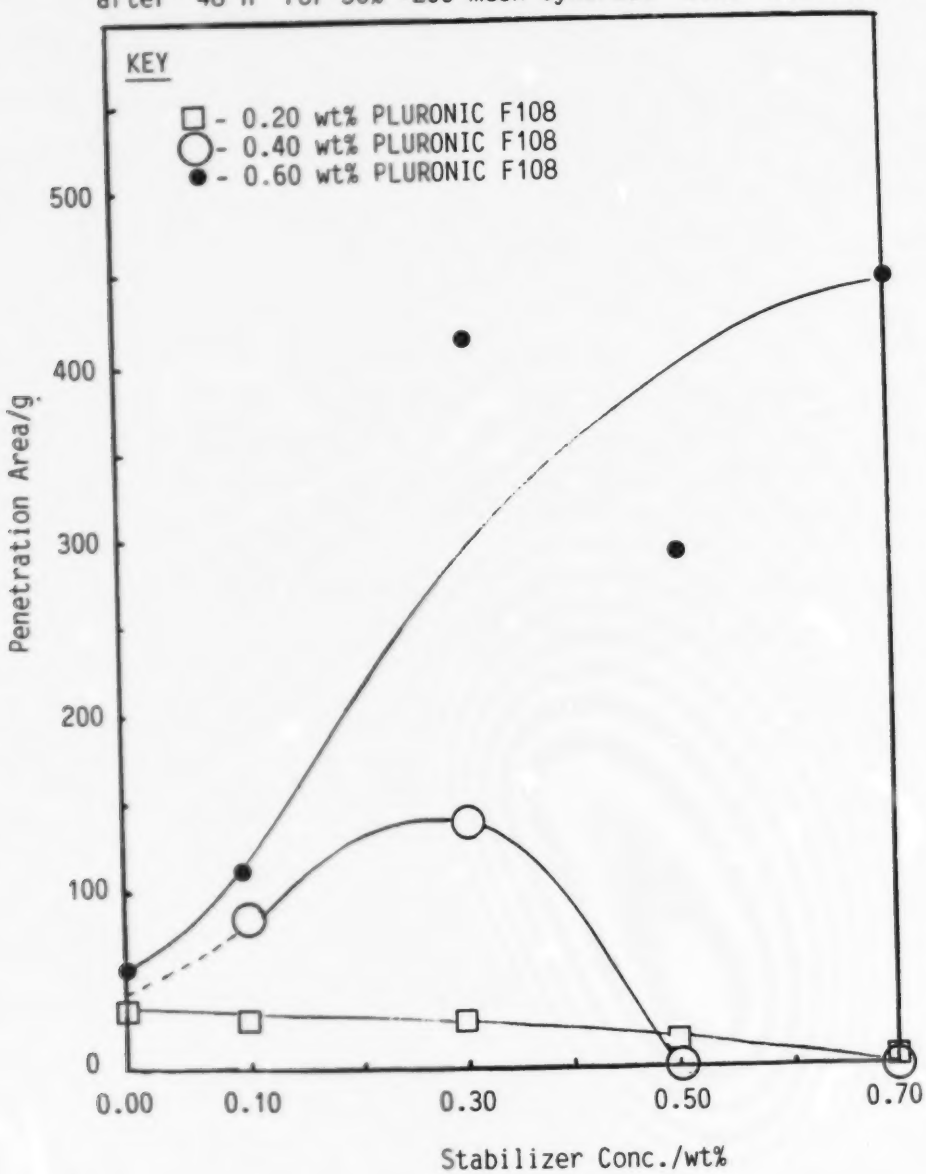
8.3 Discussion And Results

8.3.1 Evaluation Of Slurries Containing "50% -200 Mesh" Syncrude Coke

8.3.1.1 Effect Of Wyoming Bentonite

Figure 8.1 shows the penetration area after 48 h, A(48) (see reference (19)), for slurries containing 60 wt% "50% -200 mesh" Syncrude coke and three concentrations of PLURONIC F108 as a function of the concentration of Wyoming bentonite. It is clear from figure 8.1 that increasing the concentration of Wyoming bentonite from 0 to 0.70 wt% results in a gradual reduction in A(48) from 35 to 3.5 g in slurries

Figure 8.1 Effect of Wyoming bentonite concentration on penetration time after 48 h for 50% -200 mesh Syncrude coke slurries .



containing 0.20 wt% PLURONIC F108. Slurries that contain such a low concentration of surfactant are highly flocculated systems. Although they resist settling as a result of flocculation, nevertheless a small degree of settling does occur. This would lead to somewhat more compact sediments with higher mechanical strength. Consequently, it is likely that the presence of Wyoming bentonite inhibits such settling yielding a bulkier sediment with a lower mechanical strength.

The nature of the sediments in slurries that contained 0.40 wt% surfactant was very sensitive to the concentration of Wyoming bentonite that was employed. If the concentration of bentonite was between 0 and 0.30 wt%, the sediments were hard packed and exhibited a high mechanical strength. In fact A(48) increases rapidly with increasing bentonite concentration until it reaches a maximum at a bentonite concentration of about 0.30 wt%. Wyoming bentonite depends on flocculation of the clay particles to provide stability. It is likely that the degree of flocculation is insufficient at low bentonite concentrations to significantly impede settling of the coke particles. The bentonite particles would then settle out with the coke possibly permitting more efficient packing. This would in turn produce a sediment with a higher mechanical strength. Thus, it would be extremely undesirable to employ too little bentonite since this can result in a slurry which is even more unsuitable than would be the case if no bentonite were used. If the concentration of bentonite is increased above 0.30 wt%, A(48) decreases to 0 g and settling is virtually nonexistent. Such slurries demonstrated

excellent fluidity so that the rod was able to easily penetrate slurries that contained 0.50 and 0.70 wt% under its own weight in 4.0 and 2.6 S respectively.

In slurries that contained 0.60 wt% surfactant only hard packed sediments with high mechanical strengths were obtained. A(48) increased dramatically with increasing bentonite concentration. In this respect these slurries were similar to slurries that contained 0.40 wt% surfactant and between 0 and 0.30 wt% bentonite. It is likely that the same explanation that was suggested for the slurries containing 0.40 wt% surfactant is also applicable to those containing 0.60 wt%. In the latter case however, there is an even smaller degree of coke particle flocculation. Consequently, the degree of settling exhibited (and therefore A(48)) in these slurries is greater than that exhibited in slurries containing 0.40 wt% surfactant. On this basis it is clear that more than 0.70 wt% bentonite is required to stabilize "50% -200 mesh" Syncrude slurries that contain 0.60 wt% surfactant.

In past work (19) it was reported that a slurry containing: 60 wt% "50% -200 mesh" Syncrude coke, 0.60 wt% PLURONIC F108 and 0.50 wt% Wyoming bentonite had an A(336) value of 0.0g. A slurry prepared in this work gave an A(48) value of 287 g. The reasons for this discrepancy are not clear. The result reported in reference (19) represented a single slurry and while the result reported in this work is consistent with the results obtained in a series of several slurries. Thus, it is likely that

the current result is more valid than that reported in reference (19).

8.3.1.2 Effect Of Xanthan Gum

All of the slurries that were prepared with xanthan gum yielded low (less than 5 g) or zero values for A(48). Figure 8.2 shows the rod penetration time (for slurries with A(48) =0.0 g) as a function of xanthan gum concentration for three concentrations of PLURONIC F108. It is clear from figure 8.2 that there is a minimum penetration time at a xanthan gum concentration of 0.20 wt% for all three surfactant concentrations. This represents the optimum concentration of xanthan gum for all three concentrations of surfactant. The penetration times for slurries containing 0.20, 0.40 and 0.60 wt% surfactant at the optimum concentration of xanthan gum were 28.6, 21.0 and 25.7 S respectively. Thus, the optimum combination of PLURONIC F108 and xanthan gum contains 0.40 wt% PLURONIC F108 and 0.20 wt% xanthan gum.

8.3.1.3 Effect Of Guar Gum

Figure 8.3 shows the values of A(48) as a function of the concentration of guar gum for slurries continuing 0.40 and 0.60 wt% PLURONIC F108. It is clear that increasing the concentration of guar gum results in a large decrease in A(48). This type of behavior was also noted in reference (19). A(48) is 0 g in slurries containing 0.20 and

Figure 8.2 Effect of xanthan gum concentration on penetration time after 48 h for 50% -200 mesh Syncrude coke slurries .

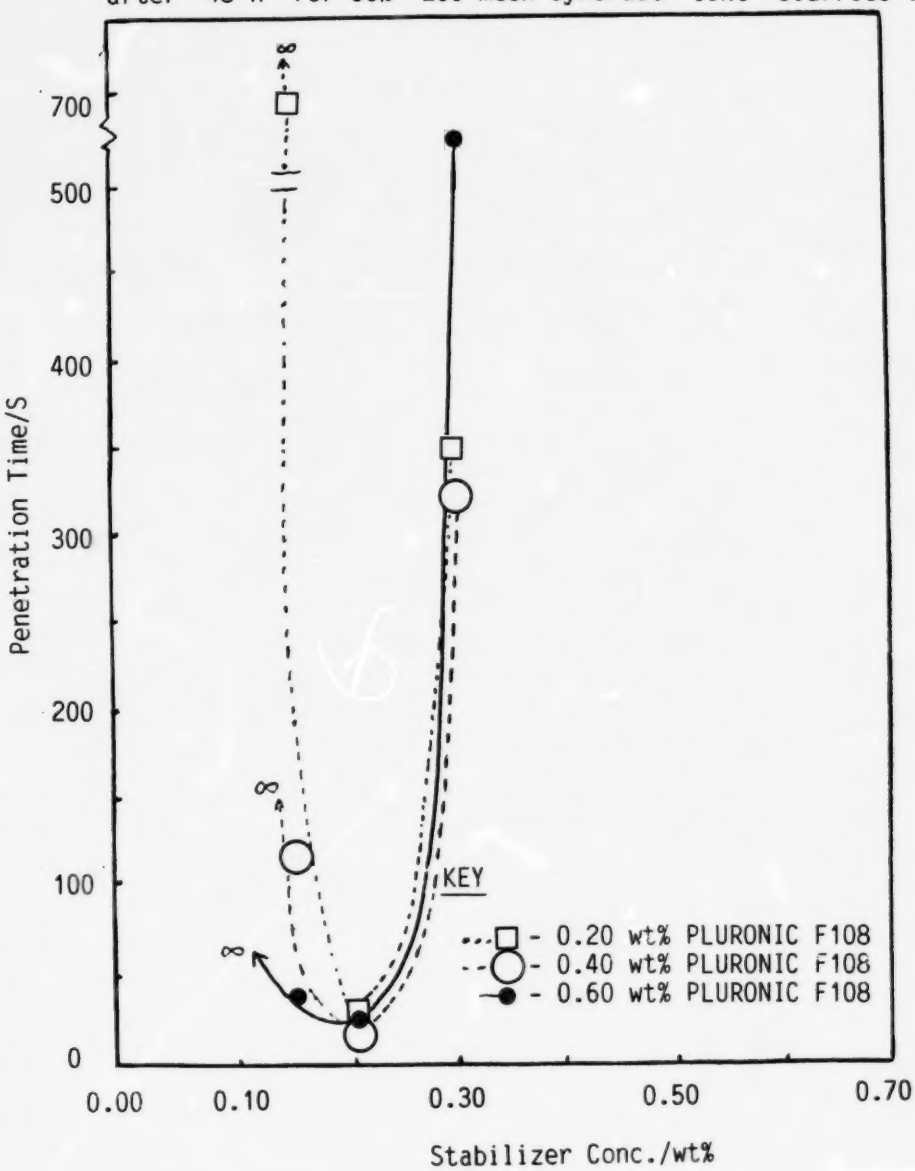
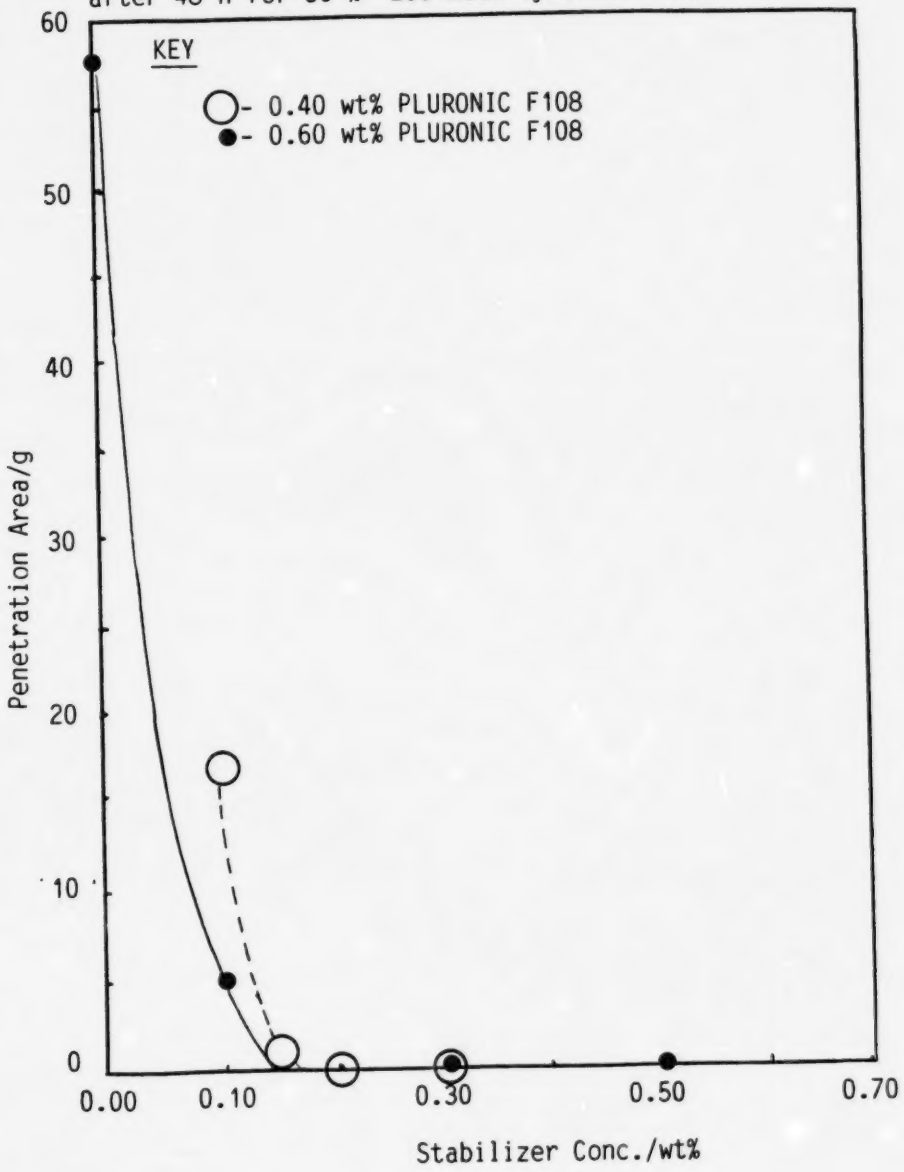


Figure 8.3 Effect of guar gum concentration on penetration area after 48 h for 50 % -200 mesh Syncrude coke.



0.30 wt% guar gum and 0.40 wt% surfactant. The corresponding penetration times for these slurries were 28.9 and 58.3 S respectively. This indicates that the optimum concentration of guar gum in slurries containing 0.40 wt% PLURONIC F108 is about 0.20 wt%

In the slurries containing 0.60 wt% surfactant A(48) becomes zero at guar gum concentrations of 0.30 and 0.50 wt%. In this case the penetration times were 10.5 and 5.6 S respectively. Clearly, more guar gum is required to reduce A(48) to 0 g in slurries that contain 0.60 wt% surfactant than in those that contain 0.40 wt% surfactant. This may be attributed to the fact that slurries that contain more surfactant are more highly deflocculated and therefore are more susceptible to settling. In this case the optimum concentration of guar gum has not been reached but it is likely to be close to 0.50 wt%.

8.3.2 Evaluation Of Slurries Containing Suncor Coke

8.3.2.1 Effect Of Xanthan Gum

Most of the slurries that were prepared with Suncor coke, xanthan gum and PLURONIC F108 had A(48) values of 0.0 g. An exception was evident in slurries that contained 0.20 wt% which were very highly flocculated. The addition of up to 0.15 wt% xanthan gum to such slurries increased A(48) from 28 to 63 g. The addition of excessive stabilizer to such a system likely results in the formation of a gel like network. Such a network can be excessively strong. Another exception was provided by a

slurry that contained 0.60 wt% surfactant and no xanthan gum. The A(48) value for this slurry was 1.8 g but the sediment was highly compact and visibly dilatant (see reference (19)). This would be very undesirable since it virtually solidifies at high shear rates.

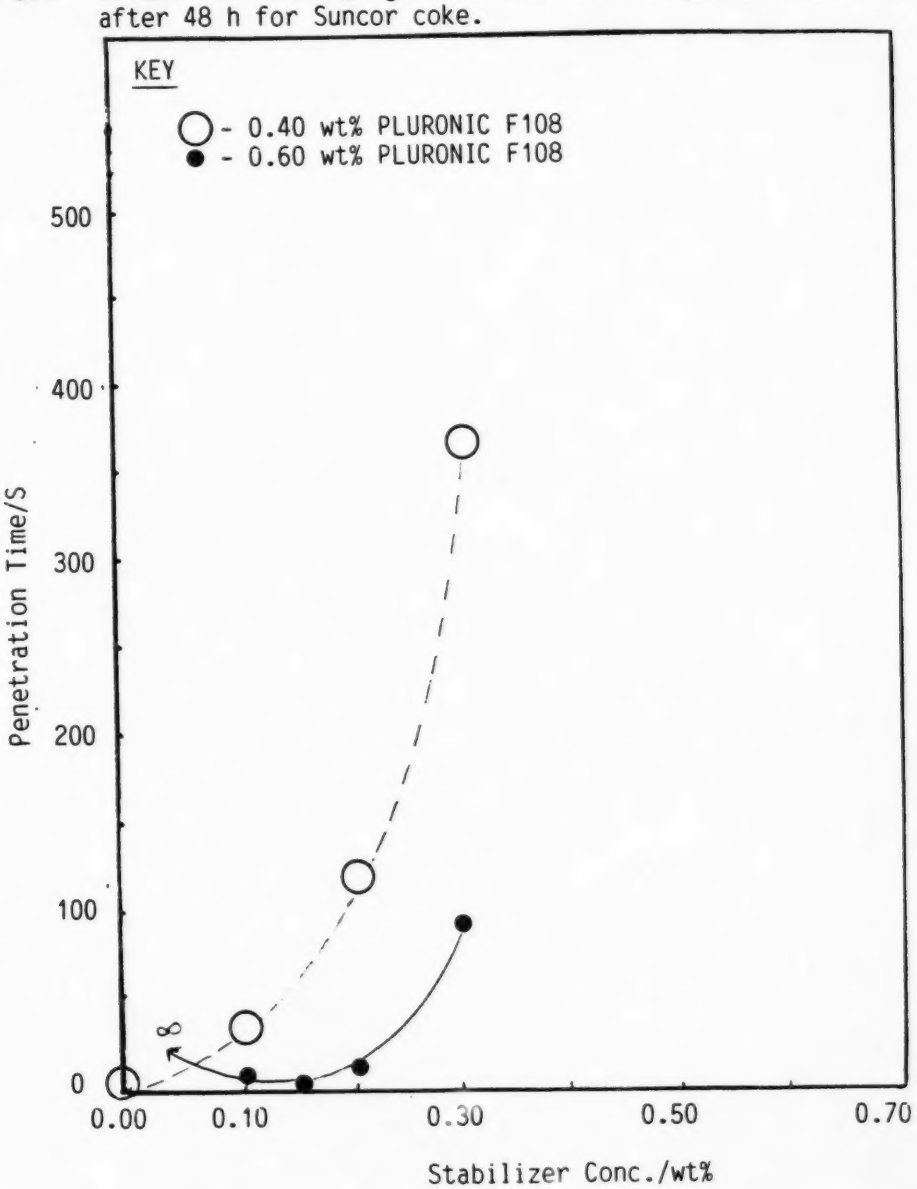
Figure 8.4 shows the penetration time as a function of xanthan gum concentration for slurries containing 0.40 and 0.60 wt% PLURONIC F108 that also yielded a value of 0.0 g for A(48). It is clear from figure 8.4 that a xanthan gum concentration of 0.10 wt% is sufficient to reduce A(48) to 0 g in slurries containing 0.60 wt% surfactant. Furthermore a minimum penetration time (and therefore the optimum concentration) occurs at a xanthan gum concentration of about 0.15 wt%.

Figure 8.4 also shows that the penetration time increases rapidly with increasing xanthan gum concentration for slurries containing 0.40 wt% surfactant. Moreover the minimum penetration time (less than 1 S) occurs in a slurry that contains 0.40 wt% surfactant and no xanthan gum. It is likely that in this slurry there is just enough flocculation to produce a network that is just strong enough to inhibit settling without significantly resisting flow.

8.3.3 Effect Of Particle Size Distribution For Syncrude Coke

Values of A(48) for slurries prepared from all three particle size

Figure 8.4 Effect of xanthan gum concentration on penetration time after 48 h for Suncor coke.



distributions of Syncrude coke are given in table 8.4. Penetration times are given in cases where A(48) is 0.0 g. Although the data are sparse, they agree with what would be expected intuitively. It is evident, from the results obtained for slurries containing 0.40 wt% surfactant, that a higher concentration of stabilizer (xanthan gum) is required to stabilize the slurry as the relative fraction of coarse (+200 mesh) particles increases. This may be attributed to a combination of two phenomena. Firstly, coarser particles would naturally require more support to prevent them from settling out than finer particles. Since there are more of them in the coarser particle size distributions, more support would be required in slurries that contain this particle size distribution.

Secondly, there seems to be a lower degree of flocculation in slurries that contain coarser particles for a given concentration of surfactant. This was indicated by the dark supernatant that was observed in the slurries that contained the "25% -200 mesh" coke - even at concentrations of surfactant that produced clear supernatants in slurries containing the other two particle size distributions. Clear supernatants are generally associated with flocculated systems (19). This may stem from the lower overall surface area that would be expected in a coarser particle size distribution. In this case a smaller amount of surfactant should sufficiently cover the particle surfaces to inhibit flocculation. This reduces the amount of surfactant that is required but would increase the amount of stabilizer that is required.

Table 8.4 Values of A(48) for "25% -200 mesh", "50% -200 mesh" and "80% -200 mesh" Syncrude coke slurries.

CONCENTRATION		PENETRATION AREA		
PLURONIC F108 wt%	XANTHAN GUM wt%	"25% -200 MESH" g	"50% -200 MESH" g	"80% -200 MESH" g
0.40	0.00	-	-	36.0
0.40	0.10	-	0.8	0.0 (5.8 S)
0.40	0.20	0.0 (315 S)	0.0 (21.0 S)	-
0.40	0.30	0.0 (16.6 S)	0.0 (321 S)	_

8.4 Conclusions

It is clear from the results presented that stable aqueous slurries of 60 wt% Syncrude fluid coke or Suncor delayed coke can be prepared using PLURONIC F108 and a stabilizer. Each of the stabilizers that were employed in this work (Wyoming bentonite, guar gum and xanthan gum) are capable greatly improving the static stability of aqueous coke slurries. However, this only occurs if a proper balance is achieved between particle settling and the stabilizing effects provided by the stabilizer and coke particle flocculation. If such a balance is not achieved , a slurry with undesirable properties will result.

Generally, an excessively high concentration of stabilizer in a highly flocculated system yields a gel like system . Such a slurry would not settle but it would also be extremely difficult to pump. The degree of flocculation can be reduced by the addition of a surfactant. If it is reduced to a point where there is insufficient flocculation to prevent settling, a very compact and possibly dilatant sediment will be formed. Settling can be inhibited by the addition of a stabilizer. To prevent settling, enough stabilizer must be added such that the support provided by the stabilizer and any residual flocculation is strong enough to suspend the coke particles. Clearly, the optimum situation occurs if there is just enough support to prevent settling without significantly impeding flow.

This situation is achieved in slurries that contain 60 wt% of "50% -200 mesh" Syncrude coke if the following concentrations of additives are employed:

(1) between 0.20 and 0.40 wt% (preferably 0.40 wt%) PLURONIC F108 and at least 0.50 wt% Wyoming bentonite.

(2) between 0.20 and 0.60 wt% (preferably 0.40 wt%) PLURONIC F108 and between 0.15 and 0.30 wt% (preferably 0.20 wt%) xanthan gum.

(3) between 0.40 and 0.60 wt% PLURONIC F108 and between 0.30 and 0.50 wt% guar gum. If 0.40 wt% PLURONIC F108 is used then it is preferable to use 0.30 wt% guar gum.

The preferred formulation for a slurry that contains 60 wt% Suncor coke (84% passing through a 200 mesh screen) contains 0.40 wt% PLURONIC F108 and no stabilizer. The preferred concentration of stabilizer for a given concentration of surfactant, increases as the fraction of coarse (+200 mesh) particles increases. Thus, the preferred concentration of xanthan gum for slurries that contain 0.40 wt% PLURONIC F108 and 60 wt% of "80% -200 mesh", "50% -200 mesh" or "25% -200 mesh" Syncrude coke are 0.10, 0.20 and 0.30 wt% respectively. More work would be required to optimize the particle size distribution.

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APPENDIX A
GENERAL RECOMMENDATIONS

On the basis of the work carried out between September 1, 1985 to September 1, 1986, the following recommendations are made:

(1) Low cost waste materials are not likely to be effective replacements for commercially available surfactants.

(2) Intense ultrasound, as it was applied in this work, is not as effective as mechanical mixing for dispersing coke in concentrated slurries.

(3) The preferred surfactant is a commercial, long chain, nonionic surfactant such as PLURONIC F108.

(4) Care must be $exercised to ensure that the optimum concentrations of additives are employed. Failure to do so may be wasteful and can yield a slurry with very undesirable properties.

(5) If natural gums are used as stabilizers, the slurries must not be stored for more than one week unless a preservative is added to prevent biological degradation.

(7) The following slurry formulations are preferred and yield fluid slurries that are stable for at least 48 h:

(I) SLURRIES CONTAINING 60 wt% "50% -200 MESH" SYNCRUDE COKE

(a) between 0.20 and 0.40 wt% (preferably 0.40 wt%) PLURONIC F108 and at least 0.50 wt% Wyoming bentonite.

(b) between 0.20 and 0.60 (preferably 0.40 wt%) PLURONIC F108 and between 0.15 and 0.30 wt% (preferably 0.20 wt%) xanthan gum.

(c) between 0.40 and 0.60 wt% (preferably 0.40 wt%) PLURONIC F108 and between 0.30 and 0.50 wt% guar gum. If 0.40 wt% PLURONIC F108 is used, it is preferable to use 0.30 wt% guar gum.

(d) 0.60 wt% PLURONIC F108 and a mixture of guar and xanthan gums with a total gum concentration of between 0.10 wt% (0.06 wt% guar gum + 0.04 wt% xanthan gum) and 0.30 wt% (0.18 wt% guar gum + 0.12 wt% xanthan gum).

(II) SLURRIES CONTAINING 65 wt% "50% -200 MESH" SYNCRUDE COKE

(a) 0.60 wt% PLURONIC F108 and 0.30 wt% guar gum.

(III) SLURRIES CONTAINING 70 wt% "50% -200 MESH" SYNCRUDE COKE

(a) 0.60 wt% PLURONIC F108 and 0.10 wt% guar gum.

(b) 0.60 wt% PLURONIC F108 and a mixture of guar and xanthan gums with a total gum concentration of 0.10 wt% (0.06 wt% guar gum + 0.04 wt% xanthan gum.

(IV) SLURRIES CONTAINING 60 wt% "25% -200 MESH" SYNCRUDE COKE

(a) 0.40 wt% PLURONIC F108 and 0.30 wt% xanthan gum.

(V) SLURRIES CONTAINING 60 wt% "80% -200 MESH" SYNCRUDE COKE

(a) 0.40 wt% PLURONIC F108 and 0.10 wt% xanthan gum.

(VI) SLURRIES CONTAINING 60 wt% SUNCOR COKE (84% -200 MESH)

(a) 0.40 wt% PLURONIC F108 and no stabilizer.

APPENDIX B
SUPPLIERS OF ADDITIVES

The following list of additive suppliers was compiled from references (b.1) and (b.2) (both of these references are available at the CANMET library in Ottawa). However, this is only a partial listing and the reader is directed to references (b.1) and (b.2) for a more complete listing of suppliers and product details.

LIST OF ADDITIVE SUPPLIERS

ADDITIVE	SUPPLIER NO.
SURFACTANTS	
Nonionic	1-7 (many others)
Anionic	5-8 (many others)
Lignosulfonates	8
STABILIZERS	
Colloidal Clays	9
Bentonite Clay	10-19
Drilling Mud	8*,13,15,18-26
Water Soluble Gums	14,27,28,29*,30,31*,32-34
Industrial Gums	14,28,31*,33,37,38*,41,42
Synthetic Gums	17,37,41
Guar Gum	14,17-19,22,27,28,29*,30,33-37, 39,40
Xanthan Gum	14,27,36,37,39

* manufactures product in Canada.
Supplier numbers correspond to entries in the index of additive suppliers that follows.

INDEX OF ADDITIVE SUPPLIERS

SUPPLIER NO.	SUPPLIER
1	B.A.S.F. Canada Inc., 5850 Cote De Liesse Rd., Montreal, P.Q. (514)-341-5411
2	Domtar Inc., (GAF Quebec) 104 Doyon Ave., Pointe Claire, P.Q. 514-697-4240
3	Rohm and Haas (Canada) Ltd., West Hill, Ont. (416)-284-4711
4	Mazer Chemicals (Canada) Inc., 2 Robert Speck Parkway, Suite 750, Mississauga, Ont. L4Z 1H8 (416)-848-2500
5	Dupont Canada Inc., Box 2200, Mississauga, Ont. (416)-821-3300 Agent: Toronto (416)-362-5621 Montreal (514)-397-2700
6	3M Canada Inc., P.O. Box 5757, London, Ont. N6A 4T1 (519)-451-2500 Agent: North York (416)-449-8010 Ottawa (613)-741-2007
7	Diamond Shamrock Canada Ltd., P.O. Box 784, Hamilton, Ont. L8N 3M8 (416)-525-4660

SUPPLIER NO.	SUPPLIER
8	Reed Lignin, Box 2025, 10 Blvd. Des Capucins, Quebec, P.Q. G1K 7N1 (416)-624-7976 Agent: Dorval (514)-636-6921
9	Engelhard Industries of Canada Ltd., 100 Engelhard Dr., Aurora, Ont. L4G 3N1 (416)-727-3191 Agent: Montreal (514)-695-3124
10	Allied Colloids (Canada) Inc., 11 Automatic Rd., Brampton, Ont. L6S 4K6 (416)-793-9473 Agent: Quebec (418)-627-3158
11	Dow Chemical Canada Inc., Modeland Rd., Box 1012, Sarnia, Ont. N7T 7K7 (519)-339-3131
12	L.V. Lomas Chemical Co., Ltd., 6365 Northwest Dr., Mississauga, Ont. L4V 1J8 (416)-677-6781 Agent: Montreal (514)-683-0660
13	Prairie Industrial Chemicals Inc., P.O. Box 7205, Saskatoon, Sask. S7K 4J2 (306)-664-2522 Agent: Winnipeg (204)-475-6261

SUPPLIER NO.	SUPPLIER
14	Prescott and Co. (Canada) Ltd., 4626 Burgoyne St., Mississauga, Ont. L4W 1G1 (416)-624-4820 Agent: Montreal (514)-735-6191
15	St. Lawrence Chemical Inc., 5405 Pare St., Montreal, P.Q. H4P 1P7 (514)-731-3628 Agent: Rexdale (416)-675-2074
16	R.T. Vanderbilt Co., Ltd., 1400 Trans Canada Hwy., Dorval, P.Q. H9P 1H7
17	A%C American Chemical Ltd., 3010 De Baene St., H4S 1L2 (514)-336-1493 Agent: Toronto 1-(800)-361-9234
18	C-I-L Inc., C-I-L House, 90 Sheppard Ave. East, North York, Ont. M2H 6H2 (416)-229-7000 Agent: Montreal (514)-397-6000
19	Mackenzie and Feimann Ltd., 311-255 W. First St., North Vancouver, B.C. V7M 3G8 (604)-980-7055 Agent: Toronto (416)-844-2970 Montreal (514)-613-9800
20	Harrison and Crossfield (Canada) Ltd., 160 Lesmill Rd., Don Mills, Ont. M3B 2T7 (416)-445-7050 Agent: (514)-748-7911

SUPPLIER NO.	SUPPLIER
21	Hoechst Canada Inc., 4045 Cote Vertu Blvd., Montreal, P.Q. H4R 1R6 (514)-333-3500 Agent: Toronto (416)-497-4700
22	Kingsley and Keith (Canada) Inc., P.O. Box 555, Etobicoke, Ont. M9C 5B1 (416)-626-8383 Agent: (514)-487-1550
23	Petrolite Canada Inc., Industrial Chemicals Group, 150 Lakeside Rd. West, Suite 23, Mississauga, Ont. L5H 1G1 (416)-461-0844 Agent: Montreal (514)-645-9150
24	Punda Inc., 310 Victoria Ave., Suite 306, Montreal, P.Q. H3Z 2M9 (514)-489-7278
25	Union Carbide Canada Inc., 123 Eglington Ave. East, Seventh Floor, Toronto, Ont. M4P 1J3 (416)-488-1444
26	Van Waters and Rogers Ltd., 9800 Van Horne Way, Richmond, B.C. V6X 1W5 (604)-273-1441 Agent: Toronto (416)-741-9190 Montreal (514)-342-9124

SUPPLIER NO.	SUPPLIER
27	Daminco Inc., 977 Pantera Dr., Mississauga, Ont. L4W 2W6 (416)-624-5414 Agent: Dorval (514)-636-6921
28	Frank E. Dempsey and Sons Ltd., 47 Davies Ave., Toronto, Ont. M4M 2A9 (416)-278-0874 Agent: Montreal (514)-636-4953
29	Henkel Chemicals Canada Ltd., 9550 Blvd. Ray Lawson, Ville D'Anjou, P.Q. H1J 1L3 (514)-353-7550 Agent: Mississauga (416)-677-3400
30	Henley Chemicals Ltd., 420 Finchdene Square, Scarborough, Ont. M1X 1C2 Agent: Montreal (514)-382-3254 or (514)-662-1739
31	Industrial Adhesives Division of Timinco Ltd., 90 Tycos Dr., Toronto, Ont. M6B 1W2 (416)-781-6113 Agent: Montreal (514)-695-8110
32	Kelco Specialty Colloids Ltd., Suite 630, 70 University Ave., Toronto, Ont. M5J 2M4 (416)-593-5730 Agent: (514)-284-4132

SUPPLIER NO.	SUPPLIER
33	Charles Tennant and Co. (Canada) Inc., Ltd., 34 Clayson Rd., Weston, Ont. M9M 2G8 (416)-741-9264 Agent: Montreal (514)-683-3295
34	Hercules Canada Inc., 4 Robert Speck Parkway, Mississauga, Ont. L4Z 1S1 (416)-868-1800 Agent: Montreal (514)-284-3430
35	Chemroy Chemicals Ltd., 2401 Anson Dr., Mississauga, Ont. L5S 1G1 (416)-677-0701 Agent: Montreal (514)-342-9124
36	Debro Inc., Chemicals Division, 7 Blair Dr., Brampton, Ont. L6T 2H4 (416)-453-7983 Agent: Montreal (514)-684-9775
37	May and Baker Canada Inc., 6557 Mississauga Rd., Mississauga, Ont. L5N 1A6 (416)-821-4450 Agent: Montreal (514)-334-7790
38	H.B. Fuller Canada Inc., 88 Industrial Blvd., Boucherville, P.Q. J4B 2X2 (514)-655-1306 Agent: Mississauga (416)-274-1238

SUPPLIER NO.	SUPPLIER
39	Stecko Chem Inc., 207 Place Frontenac, Suite 8, Pointe Claire, P.Q. H9R 4Z7 (514)-697-6901
40	Virchem Canada Inc. 151 Randall Ave., Oakville, Ont. L6J 1P5 (416)-842-4092
41	Halltech Inc., 465 Coronation Dr., West Hill, Ont. M1E 2K2 (416)-284-6111

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